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RELATIONSHIP OF RESIDUE FORMATION TO WAX
USED IN M203 PROPELLING CHARGE LINERS

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DECEMBER 1979



US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
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The results of the test firings were consistent with the proposed mechanism for liner breakup. The charges made with Polywax 655 produced the least residue under all conditions. Factors other than the choice of wax which increased residue frequency were: higher tube temperature, longer chambering time, rayon/lead laminate as the liner substrate, and increased amounts of dacron staple in the liner. Since these factors tend to decrease liner brittleness, their effect is consistent with the proposed mechanism for liner breakup and residue formation. Charges using Polywax 655/scrim in the liner have been shown to be free of residue when fired in gun tubes up to 149°C (300°F) with chambering times under 30 seconds.

SUMMARY

Recurrence of residue problems with the 155 mm M203 propelling charges led to an investigation of the wax used in the wear-reducing additive liner. Laboratory investigations indicated that the currently used wax, Indramic 170C[®], softens substantially under firing conditions; whereas Polywax 655[®] is substantially more brittle. A mechanism for liner breakup is proposed which suggests that, at the temperatures encountered during firing, a more brittle liner would be more effectively dispersed and the frequency of residue would be reduced. The brittleness of the liner is determined principally by the melting characteristics of the wax used in the liner. These characteristics are best determined by laboratory tests of which Differential Scanning Calorimetry (DSC) is the most useful.

The results of gun firings were consistent with the proposed mechanism for liner breakup, and the laboratory tests used to characterize liner waxes. Charges made with Polywax 655, which were characterized by DSC as most brittle under gun firing conditions, produced the least residue under all conditions. The brittleness of Polywax 655 results from the high degree of crystallinity of the constituent straight chain low-molecular-weight polyethylene molecules in the orthorhombic structure. Other factors which increased residue frequency were: higher tube temperature, longer chambering time, rayon/lead laminate as the liner substrate, and increased amounts of dacron staple in the liner. Since these factors tend to decrease liner brittleness, their effect is consistent with the proposed mechanism for liner breakup and residue formation. Charges using Polywax 655/scrim in the liner have been shown to be free of residue when fired in gun tubes up to 149°C (300°F) with chambering times under 30 seconds.

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INTRODUCTION

Wear-reducing additive liners for the M203 propelling charge contain approximately 53.5% wax, 46% titanium dioxide, and 0.5% dacron fiber. Prior to the production of propelling charge lot 79A-069807, paraffin wax with a 71°C (160°F) drop melting point was used in the additive. Following an investigation of the occurrence of cloth residue in hot gun tubes [greater than 71°C (160°F)] after firing charges conditioned at 63°C (145°F), a microcrystalline wax with a higher drop melting point wax was substituted (refs. 1,2). This modification eliminated the residue problem exhibited by the 79A-069807 lot for those particular conditions. However, during recent 155 mm weapon test programs which used lot 79A-069807, e.g., M109A2/A3 firing table test and M198 PVT, cloth residue was again reported. The residue was observed after charges, conditioned at ambient temperature, were fired in both cool and hot gun tubes. Since the original problem was effectively solved by changing the wax, a more concentrated study of wax was undertaken.

This report summarizes the key findings of the expanded study of wax and the implications for understanding and resolving the residue problem. The background to the residue problem, the results of the gun firings and laboratory tests, and the current status of the M203 propelling charge are given in references 1 and 2.

TEST RESULTS

Additive liners for the 79A-069807 lot of M203 propelling charges were produced with the microcrystalline wax Indramic 170C®. This wax, which is also used as a desensitizer in some cast and pressed explosive compositions, is specified by MIL-W-20553D which describes the required acceptance tests. One of the most informative specification tests, for purposes of this study, is Differential Scanning Calorimetry (DSC). This test measures the heat gained or released by a sample relative to a standard as its temperature is changed at a constant, predetermined rate. DSC heating traces for several waxes investigated are shown in figures 1 through 4.

Shell 300® is representative of the paraffin waxes used before the production of lot 79A069807, Indramic 170C® is the current "high melt point" wax and the low-molecular-weight polyethylene synthetics, Polywaxes 500 and 655®, are representative of waxes considered for future use. Analysis of these data yields the initial melting and liquefaction points and the heat of fusion, which are listed in table 1, with the drop melting point and penetration. Penetration is the distance in units of 0.1 mm which

a specially prepared, weighted needle sinks into the wax at a given temperature within a given time. Penetration data were obtained according to procedures in ASTM D-1321.

DISCUSSION

Wax Properties

The results of the laboratory test can be understood best in terms of the basic properties of the waxes (refs. 3,4,5). Shell 300 and Indramic 170C are both obtained from the highest-molecular-weight fractions of petroleum. Petroleum wax is classed as paraffin or microcrystalline according to the method by which the wax is separated from the petroleum. Paraffin waxes such as Shell 300® are processed from the distillation products of crude petroleum; whereas, microcrystalline waxes (such as Indramic 170C) are processed from the fraction of petroleum remaining after distillation. Since they are distilled, paraffin waxes contain a narrower range of hydrocarbons of lower molecular weight than microcrystalline waxes. Paraffin waxes contain a higher ratio of straight-chain to branched hydrocarbons. The straight chain and more symmetrical hydrocarbons form crystalline solids (paraffin wax is sometimes termed macrocrystalline wax) with higher melting points than the less symmetrical hydrocarbons.

At room temperature, paraffin waxes (C_{18} to C_{36}) are orthorhombic in structure. The long, normal paraffin molecules are arranged perpendicular to the flat upper and lower faces of thin rhombic plates. At higher temperatures, the molecules rotate about their long axis to acquire cylindrical symmetry and undergo exothermic transition to an hexagonal structure. The wax is flexible, ductile, and soft in this hexagonal structure. The phase transition occurs nearer to the melting point with increasing molecular weight and ceases to exist above C_{30} .

Because microcrystalline waxes (C_{40} to C_{60}) have a higher percentage of asymmetrical molecules, crystallization into the orthorhombic structure by the symmetrical molecules is not normal. The small, needlelike crystals formed are surrounded by amorphous material resulting from hydrocarbons so asymmetrical that they cannot crystallize. Thus, microcrystalline wax usually has a broader molecular weight range and is softer than paraffin wax of a comparable melting point.

Polywax 500 and 655 (manufactured by the Bareco Division of Petrolite, Incorporated) are low-molecular-weight homopolymers of ethylene. The polyethylene is completely straight chain with a very narrow molecular weight distribution¹. The polywaxes have the crystallinity and brittleness of paraffin wax with the high melting point of microcrystalline wax. Since Polywaxes are synthesized, their properties do not vary because of changes in the petroleum source.

Laboratory Results

The properties of the waxes given in table 1 are readily understandable in terms of the types of waxes tested. The microcrystalline wax Indramic 170C, although it has a higher liquefaction point than the Shell 300, which it replaced, is softer according to the penetration test and has a broader melting range. Although it has nearly the same liquefaction point as Indramic 170C, Polywax 500 is harder since it mimics paraffin wax. Polywax 655 has the highest liquefaction point and is hardest.

In addition to providing some of the characteristics shown in table 1, the DSC trace reflects the melting process for the wax. As figures 1 through 4 illustrate, these waxes melt over a wide temperature range. This occurs because waxes are composed of a characteristic distribution of molecules. Structure in the DSC trace is indicative of the various molecular weight fractions. For example, the molecular weight distribution in Indramic 170C (fig. 5) indicates two peaks in the distribution which correspond to the two peaks observed in the DSC trace.

The liquefaction point corresponds roughly to the drop melting point measured according to ASTM Method D127. Up to that point, fractional melting softens the wax. A quantitative measure of softening is obtained from penetration tests at various temperatures.

A more graphic method of comparing the fractional melting of several waxes is to plot the relative fractional heat absorption as a function of temperature. This is obtained by normalizing the integral of the DSC trace up to a given temperature with respect to

¹The polydispersity, which is defined as the weight-average molecular weight divided by the number-average molecular weight, is less than 1.3.

the total heat absorbed. The result (fig. 6) indicates, for example, that the Indramic 170C wax has a higher fraction melted, up to 68°C (155°F), than all the other waxes tested. In fact, the amount of additional heat required to completely melt Indramic 170C is only 14.5 calories per gram versus 29 calories per gram for Shell 300.

Between 68°C (155°F) and the liquefaction point, Indramic 170C has a lower fraction melted than shell 300. This inversion is due to the double peak in the Indramic 170C DSC. Polywax 500, although it has nearly the same liquefaction point as Indramic 170C, clearly has a lower fractional melting percentage. Polywax 655 exhibits additional lowering of the fractional melting with respect to the other waxes studied.

The exotherm, due to the transition to the hexagonal structure, is difficult to observe for a composite of hydrocarbons such as that present in these waxes. The hexagonal structure must play some part in softening, particularly of the lower melting paraffin waxes such as Shell 300.

There is no direct experimental evidence to indicate exactly how the additive liner functions in the gun, i.e., whether it is broken up, melted, vaporized and/or dispersed during the ballistic cycle. Other results (refs. 1,2) indicate that physical breakup of the additive is important in the mechanism. Pieces of liner were placed in a closed vessel with 155 mm M30A1 propellant to determine whether the liner would be consumed. The amounts of liner and propellant were chosen to be in the same weight percent as in the M203 charge. The closed bomb was preheated to 71°C (160°F) before the firings. Some tests were conducted with the liner loose in the vessel; in others, it was intentionally stuck to the wall. Residue consisting of the liner essentially in tact was recovered for both conditions. Wax impregnated jacket material was similarly tested, both loose and stuck, and was consumed in each case.

An erosion test fixture which is basically a closed bomb fitted with a gun barrel was used for similar tests. It was not preheated, however. When the liner was loose, some residue was ejected; when it was stuck to the wall, some residue remained in the chamber. Wax impregnated cloth was consumed whether loose or stuck to the walls.

An idealized heat flow analysis² was performed to simulate the conditions that the liner might encounter during actual gun firing. The calculation simulated immersion of a 1.2 mm thick slab of the TiO₂/wax liner initially at 300 K, in a 3000 K temperature

bath for 12.2 ms. Convective heating was not included. The calculation indicated that the center of the slab barely reached its 71°C (160°F) melting point after 12.2 ms.

Both the laboratory tests and heat flow simulation strongly suggest that, in actual gun conditions, physical breakup and convective heating are required to consume and disperse the wear additive liner. Presumably the necessary conditions are provided by the forward gas velocity and turbulence. Breakup is inhibited by the softening which accompanies fractional melting.

The following mechanism for liner functioning and the formation of residue is proposed:

1. When the initial temperature (the temperature at the time of primer function) of the additive liner is below the initial melting point of the wax, the additive liner breaks up early in the ballistic cycle, exposing a large surface area so that efficient convective heat transfer occurs, and the additive is melted, vaporized, and/or dispersed.

2. When the initial temperature of the additive liner is between the initial melting and liquefaction point, there is less breakup of the additive. Depending on the degree of softening, less surface area is exposed by breakup and melting/vaporization occurs later in the ballistic cycle. In this range, an increasing frequency of residue can be anticipated, since the softened wax can effectively penetrate and shield the adjacent cloth layers. When the initial temperature of the chambered charge increases above the liquefaction point, an increasing incidence of residue can be expected.

3. The initial temperature of the additive liner in the chambered charge is controlled by the following factors:

The temperature of the charge prior to chambering as determined either through ambient conditions or temperature conditioning.

- The change in charge temperature which occurs after chambering. The magnitude of the change increases with chambering time and the difference between charge and tube temperature.

²p. Kemmey, private communication.

If the proposed mechanism is correct, there will be less residue when the additive contains a wax which is brittle over the broadest possible temperature range. Since any wax is less brittle with increasing temperature, one would also predict that residue would increase with increases in conditioning temperature, tube temperature, and chambering time. Additionally, other components of the liner may impede liner breakup.

GUN FIRINGS

The results of M203 test firings at JPG in June and July of 1979^{3,4,5} can be used to test the proposed mechanism. The gun firings can be divided into two phases: Phase I, in which variations of the M203 charge other than those involving wax were tested, and Phase II, based on the results of Phase I, in which only variations in wax and the substrate supporting TiO₂/wax in the liner were tested as a function of tube and charge temperature.

Phase I

The results of the first series of test firings performed in June 1979 (tables 2 through 4) compare variations using Indramic 170C (A through H) with those using Polywax (I through L). All the groups fired are variations of the M203 charge configuration used in lot 79A-069807. Groups A and B used dark and light colored Indramic 170C, respectively, and no stearyl alcohol (0% to 1% stearyl alcohol is discretionary in the specification for the liner). Groups C and D used a blend of light and dark Indramic 170C with and without stearyl alcohol, respectively. Group E is the same as D with 2.5% dacron staple (0.75% is the maximum specified). Group F is the same as D, but with a 50% increase in liner weight. Group G is the same as D, but with the rayon/lead laminate used as the substrate in the liner⁶. Group H is the same as D but using Kerr-McGee TiO₂ instead of Dupont TiO₂. Groups I and K are the same as Group A, but with Indramic 170C replaced by Polywax 500 and 655, respectively. Groups J and L are the same as Groups I and K, respectively, but with rayon/lead laminate replacing scrim. The Indramic 170C variations A through D can be

³D. Ellington, L. Harris, J. Rutkowski, Trip Report, JPG, June 1979.

⁴L. Harris and K. Russell, Trip Report, JPG, July 1979.

⁵D. Downs and D. Ellington, Trip Report, JPG, July 1979.

⁶The rayon/lead laminate is used as the substrate in the 8-inch propelling charge M188E1. Rayon is a heavier, stronger, more closely woven fabric than the scrim used in the M203.

identified with the standard charge lot 79A-069807, since waxes encompassing all these color variations were used in production.

The more brittle waxes, Polywax 500 and 655 (table 4), clearly produce the lowest frequency of residue. The increase of residue frequency with tube temperature, presumably due to softening of the wax in the chambered charge, is clearly shown by comparison of tables 2 and 3. The higher dacron content (E), which inhibits liner breakup, produces a higher frequency of residue in a tube below 82°C (180°F). The rayon/lead laminate both for Indramic 170C and Polywax 500 produces more residue than the scrim used in conventional M203 liners. The cloth used in the laminate, since it is heavier and stronger than that used in the scrim, impedes liner breakup. Since Polywax 500 (which has nearly the same drop melting point as Indramic 170C) leads to lowered residue frequency, wax characteristics other than the melting point are important.

In summary, the results of the Phase I gun firings are consistent with the premise that factors which inhibit liner breakup lead to a higher incidence of residue. Relatively softer wax, the rayon lead laminate, and increased dacron content inhibit liner breakup leading to greater frequency of residue.

Phase II

The results of the Phase I firings show an increased frequency of residue for the Indramic 170C in hot tubes [greater than 82°C (180°F)]. Phase II was designed to determine the temperature dependence of residue for polywax charges. Groups U and V are the same as standard lot 79A-069807 with Polywax 655 replacing Indramic 170C in U and V, and rayon/lead laminate replacing scrim in V.

The round-by-round results as a function of tube temperature and chambering time are given in figures 7 through 12. A summary of the results is given in tables 5 through 7. The following conclusions can be drawn:

For Polywax/scrim charges conditioned at 21°C (70°F) no residue is observed up to a temperature of 138°C (280°F) when the round is chambered for less than one minute. Longer chambering times (1 to 3 minutes) result in increased residue. The Polywax/laminates give somewhat more residue. Both Polywax variations are substantial improvements on the Indramic 170C charges.

The Polywax charges give substantially less residue per round than the Indramic 170C (table 7). As for the 21°C (70°F) charges, Polywax/scrim produces somewhat less residue than Polywax/laminate.

CONCLUSIONS

The results of gun firings with Polywax 655 charges and Indramic 170C charges are consistent with the mechanism that a more brittle liner wax, as measured by the laboratory tests described above, enhances liner breakup resulting in a decrease in residue. The Polywax/scrim charges performed somewhat better than the Polywax/laminate charges which have a stronger liner that impedes liner breakup.

The Polywax 655/scrim charges have the following advantages over Indramic 170C charges:

1. There is no residue with 21°C (70°F) conditioned Polywax 655 charges when the chambering time is less than one minute and the gun tube temperature is ambient to 138°C (280°F). Under the same conditions, Indramic 170C charges give a residue frequency of at least 40% when the gun tube temperature is greater than 93°C (200°F).

2. There is some residue with 63°C (145°F) conditioned Polywax 655 charges. However, the frequency and amount is less than one gram per round with gun tube temperatures of ambient to 149°C (300°F), whereas Indramic 170C produces 34 grams of residue per round when gun tubes are heated above 82°C (180°F).

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Table 1. Characteristics of liner waxes

	Initial melting point °C (°F)	Liquefaction point °C (°F)	Heat of fusion (cal/g)	Penetration at 43°C (110°F) (0.1 mm)	Drop melting point °C (°F)
Shell 300	12 (54)	76 (169)	49.8	30	71 (160)
Indramic 170C	3 (37)	91 (196)	42.5	45	80 (176)
Polywax 500	12 (54)	97 (207)	55.8	21	88 (191)
Polywax 655	13 (55)	109 (229)	58.9	7	102 (211)

Table 2. Results of gun firings of M203 charge variations with temperatures less than 82°C (180°F)

Group ^a	Description	Tube temperature		Rounds with residue ^b
		°C	(°F)	
A	Dark 170C, no SA	28-53	(82-127)	0
B	Light 170C, no SA	54-74	(129-166)	2
C	Blend 170C, no SA	56-82	(150-180)	1
D	Blend 170C, SA	-	-	-
E	High dacron	73-79	(164-174)	9
F	50% weight increase	58-78	(136-172)	1
G	Rayon/lead laminate	32-59	(89-139)	1
H	Kerr-McGee TiO ₂	31-56	(88-132)	0
I	Polywax 500	61-76	(142-168)	1 (2x1) ^c
J	Polywax 500/laminate	28-54	(82-129)	0
K	Polywax 655	74-77	(166-170)	0
L	Polywax 655/laminate	56-72	(132-162)	1 (2x1/2) ^c

^aSee text for explanation of group designations.

^bFrom a total of 15 rounds fired.

^cDimensions in inches.

Table 3. Results of gun firings of M203 charge variations with temperatures greater than 82°C (180°F)

<u>Group^a</u>	<u>Description</u>	<u>Tube temperature</u>		<u>Rounds with residue^b</u>
		<u>°C</u>	<u>(°F)</u>	
A	Dark 170C, no SA	100-109	(212-229)	7
B	Light 170C, no SA	90-101	(194-213)	11
C	Blend 170C, no SA	81-93	(178-200)	3
D	Blend 170C, SA	77-96	(172-204)	10
E	High dacron	-	-	-
F	50% weight increase	86-92	(187-198)	9
G	Rayon/lead laminate	92-98	(198-208)	12
H	Kerr-McGee T102	93-102	(199-216)	11
I	Polywax 500	85-102	(185-215)	1 (2x1) ^c
J	Polywax 500/laminate	104-111	(219-231)	9
K	Polywax 655	79-88	(175-191)	0
L	Polywax 655/laminate	98-106	(209-223)	0

^aSee text for explanation of group designations.

^bFrom a total of 15 rounds fired.

^cDimensions in inches.

Table 4. Residue frequency for phase I M203 charge variations

<u>Group*</u>	<u>Description</u>	<u>Rounds with residue/ total rounds</u>	<u>Freq (%)</u>
A,B,C,D	170C/scrib	34/120	28
I	500/scrib	2/30 (small)	6
K	655/scrib	0/30	0
L	655/laminate	1/30 (small)	3

*See test for explanation of group designations.

Table 5. Phase II residue summary [chamber less than 82°C (180°F)]

<u>Group*</u>	<u>Temperature</u>		<u>Rounds fired</u>	<u>Rounds with residue</u>	
				<u>Larger than 1-1/2 in.</u>	<u>Smaller than 1-1/2 in.</u>
79A-69807	°C	(°F)			
	21	(70)	10	0	1
	63	(145)	5	0	1
U (scrim)	-51	(-60)	15	0	1
	21	(70)	45	0	0
	63	(145)	15	0	1
V (laminate)	-51	(-60)	15	0	0
	21	(70)	15	0	1
	63	(145)	15	0	5

*See text for explanation of group designations.

Table 6. Residue summary [chamber greater than 82°C (180°F)]

Group ^a	Temperature		Rounds fired	Rounds with residue		Frequency of residue larger than 1-1/2 in. (%)
	°C	(°F)		Larger than 1-1/2 in.	Smaller than 1-1/2 in.	
79A-69807	21	(70)	25	10	3	40
	63	(145)	10	1	1	10
U (scrim)	21	(70)	44	2	3	5
	63	(145)	45	3	8	7
V (laminare)	21	(70)	60	3	5	5
	63	(145)	45	7	12	16
U (scrim) ^b	-51	(-60)	4	0	0	0
	63	(+145)	4	0	0	0
V (laminare) ^b	-51	(-60)	4	1	0	25
	63	(+145)	4	1	0	25

^aSee text for explanation of group designation.

^bTransportation vibration and rough handling tests.

Table 7. Average weight of residue per round
and frequency of occurrence^a

<u>Group^b</u>	<u>Charge temperature</u>		<u>Weight at temp less than 82°C (180°F)</u>		<u>Weight at temp greater than 82°C (180°F)</u>	
	°C	(°F)	g	(%)	g	(%)
79A-69807	21	(70)	<1	(10)	2.2	(40)
	63	(145)	<1	(20)	33.9	(20)
U (scrim)	21	(70)	-	(0)	<1	(7)
	63	(145)	<1	(7)	<1	(22)
V (laminated)	21	(70)	<1	(7)	<1	(13)
	63	(145)	<1	(33)	<1	(39)
A,B,C,D	21	(70)	3.2	(15)	3.2	(42)

^aTotal residue/number of rounds with residue. One gram of cloth residue is approximately 6 in.².

^bSee text for explanation of group designation.

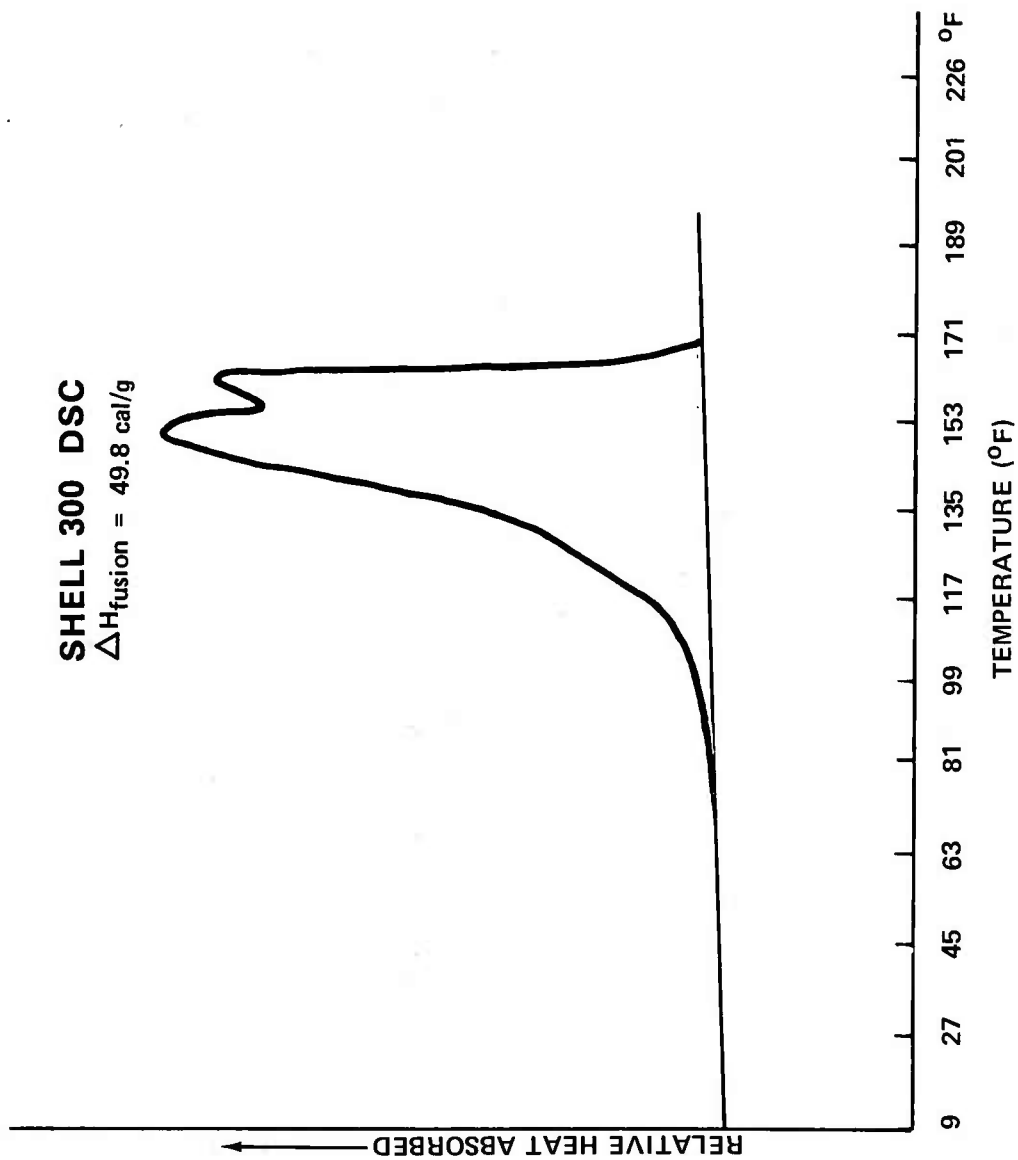


Figure 1. Shell 300 DSC.

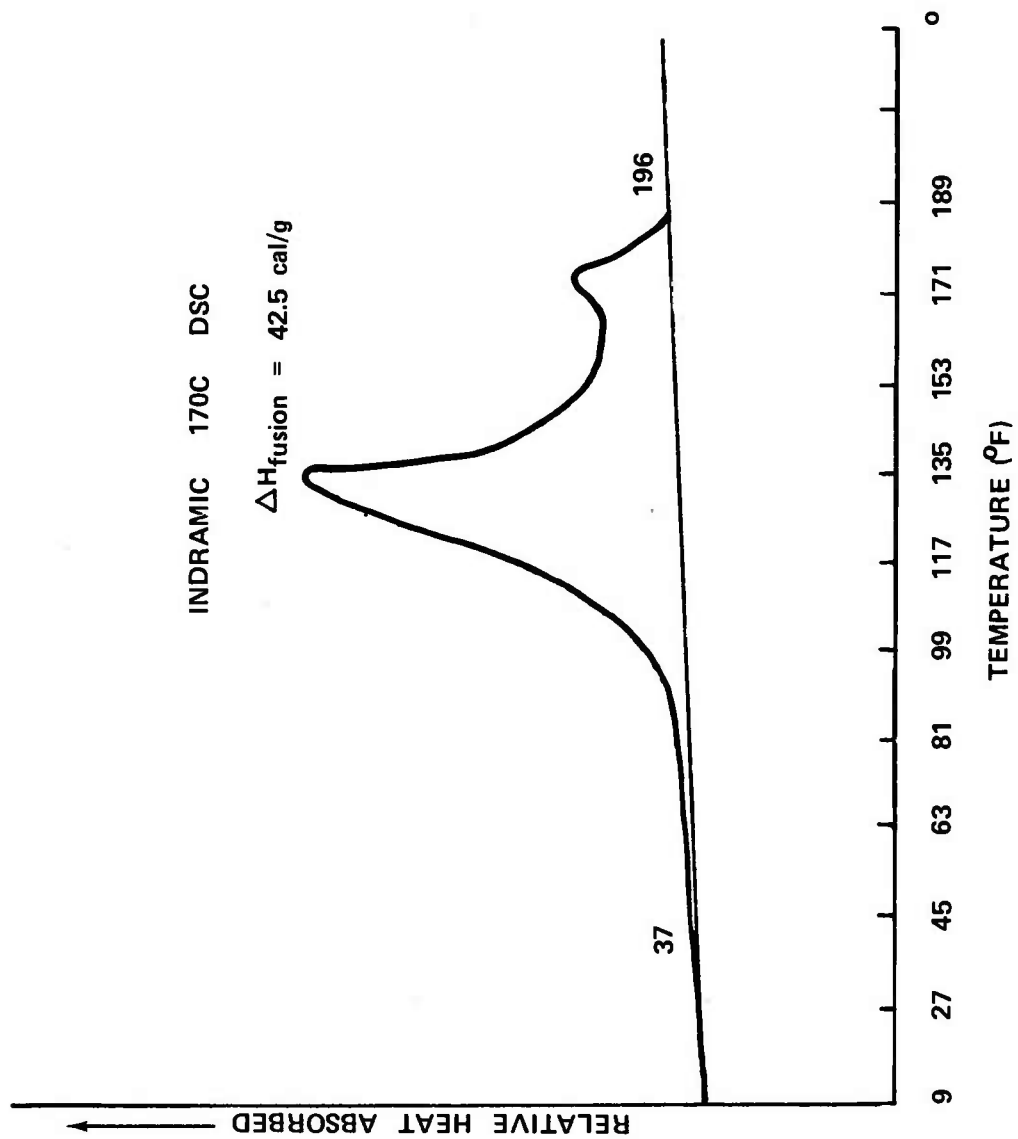


Figure 2. Indramic 170C DSC.

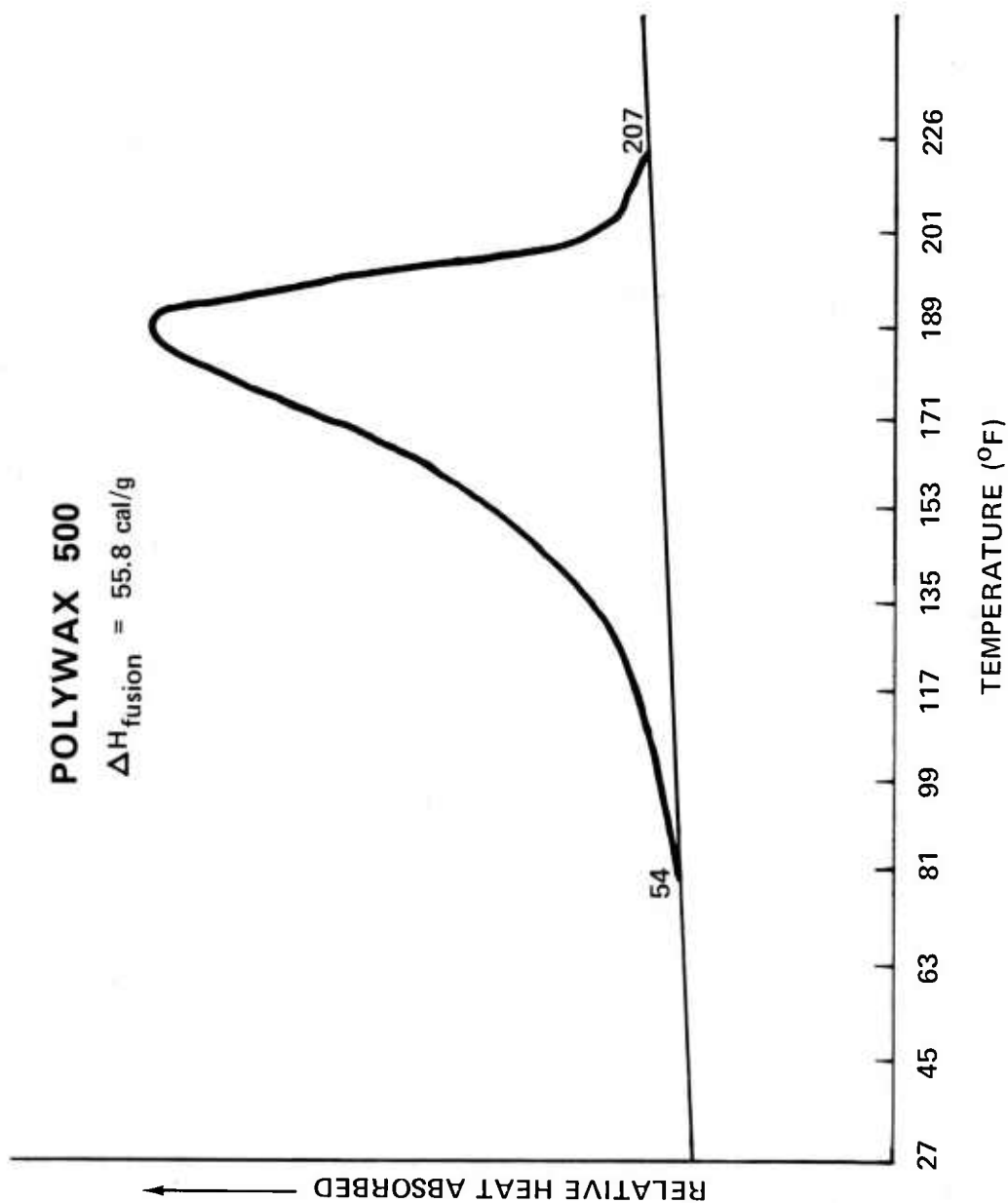


Figure 3. Polywax 500 DSC.

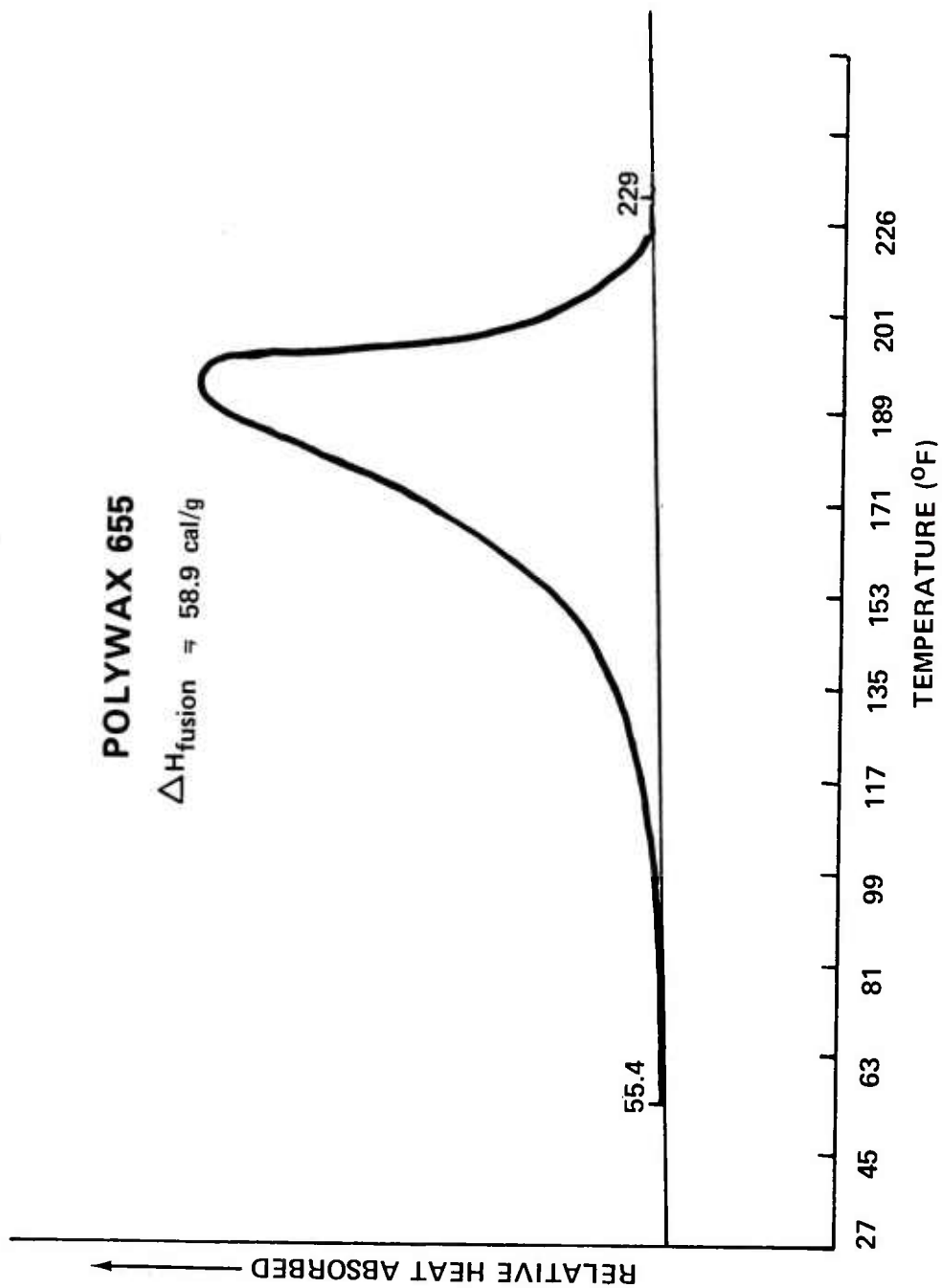


Figure 4. Polywax 655 DSC.

INDRAMIC 170C LIQUID CHROMATOGRAPHY

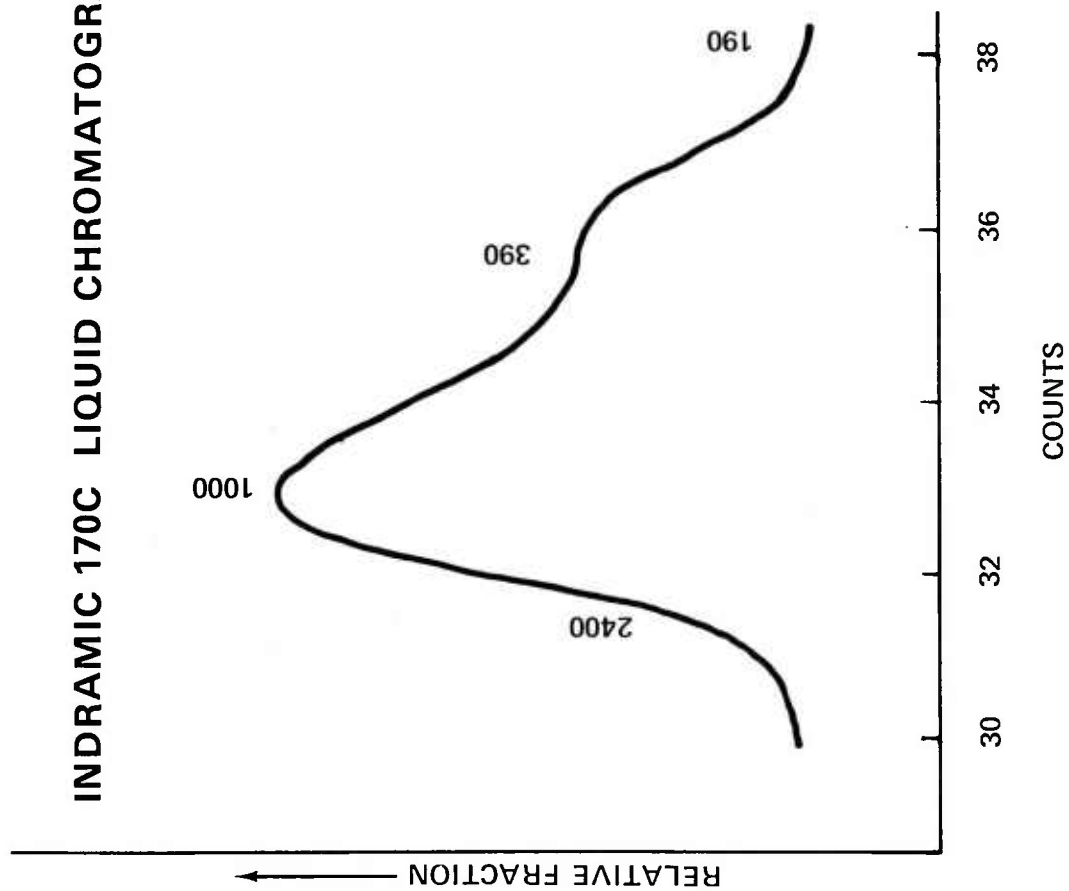


Figure 5. Indramic liquid chromatography.

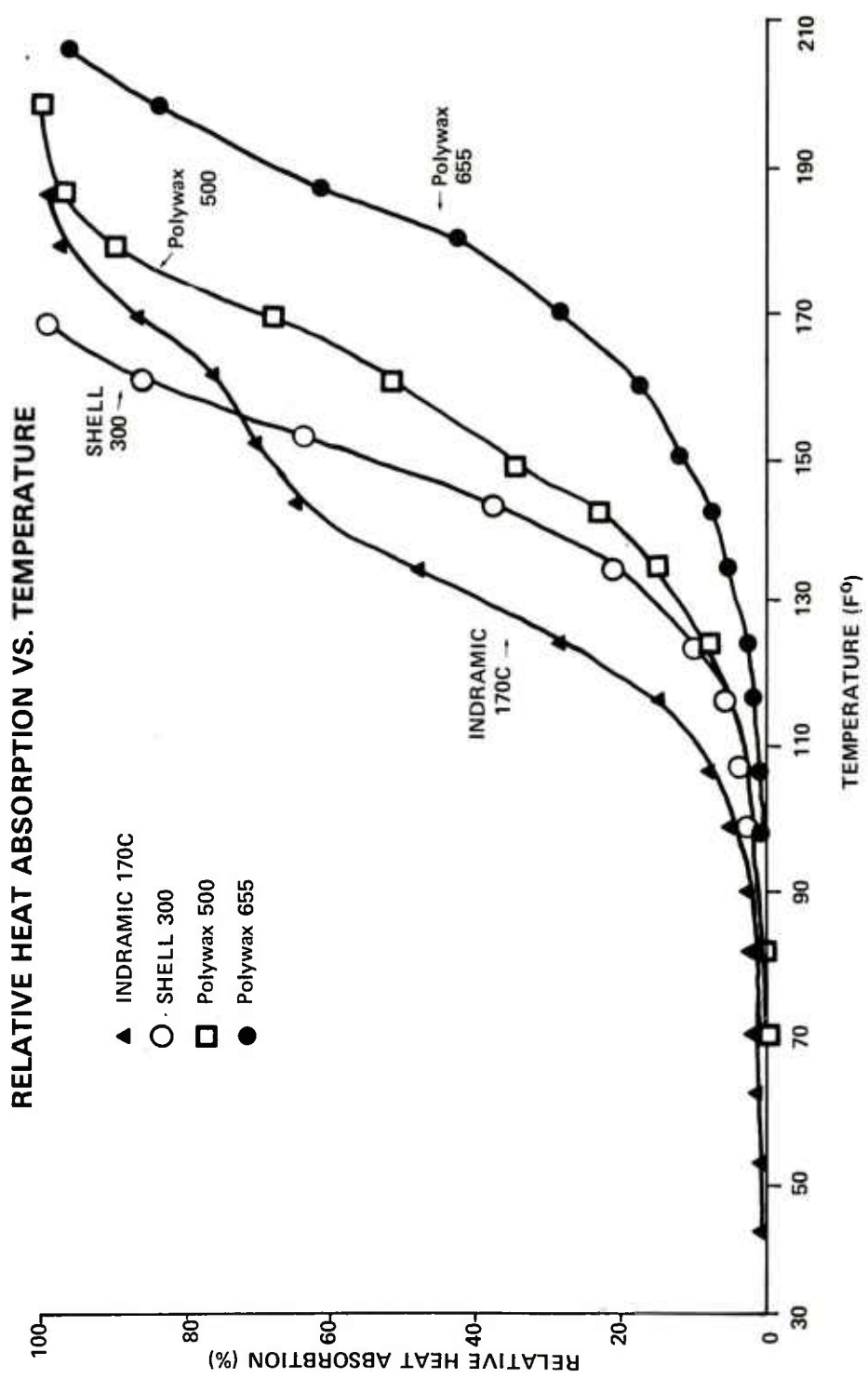


Figure 6. Integral heat absorption vs temperature.

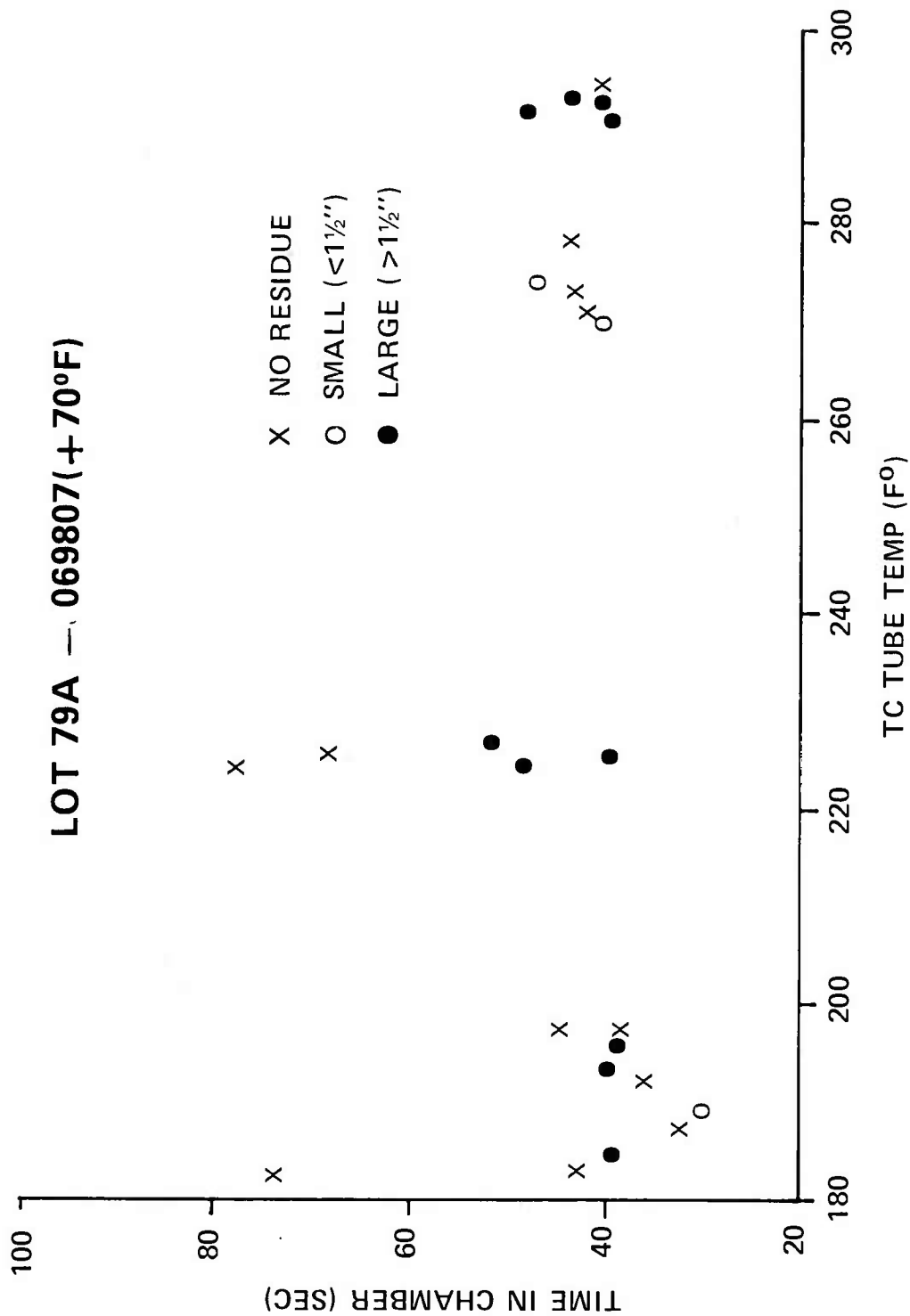


Figure 7. Indramic 170C residue frequency at 210C (70°F).

LOT 79A — 069807(145°F)

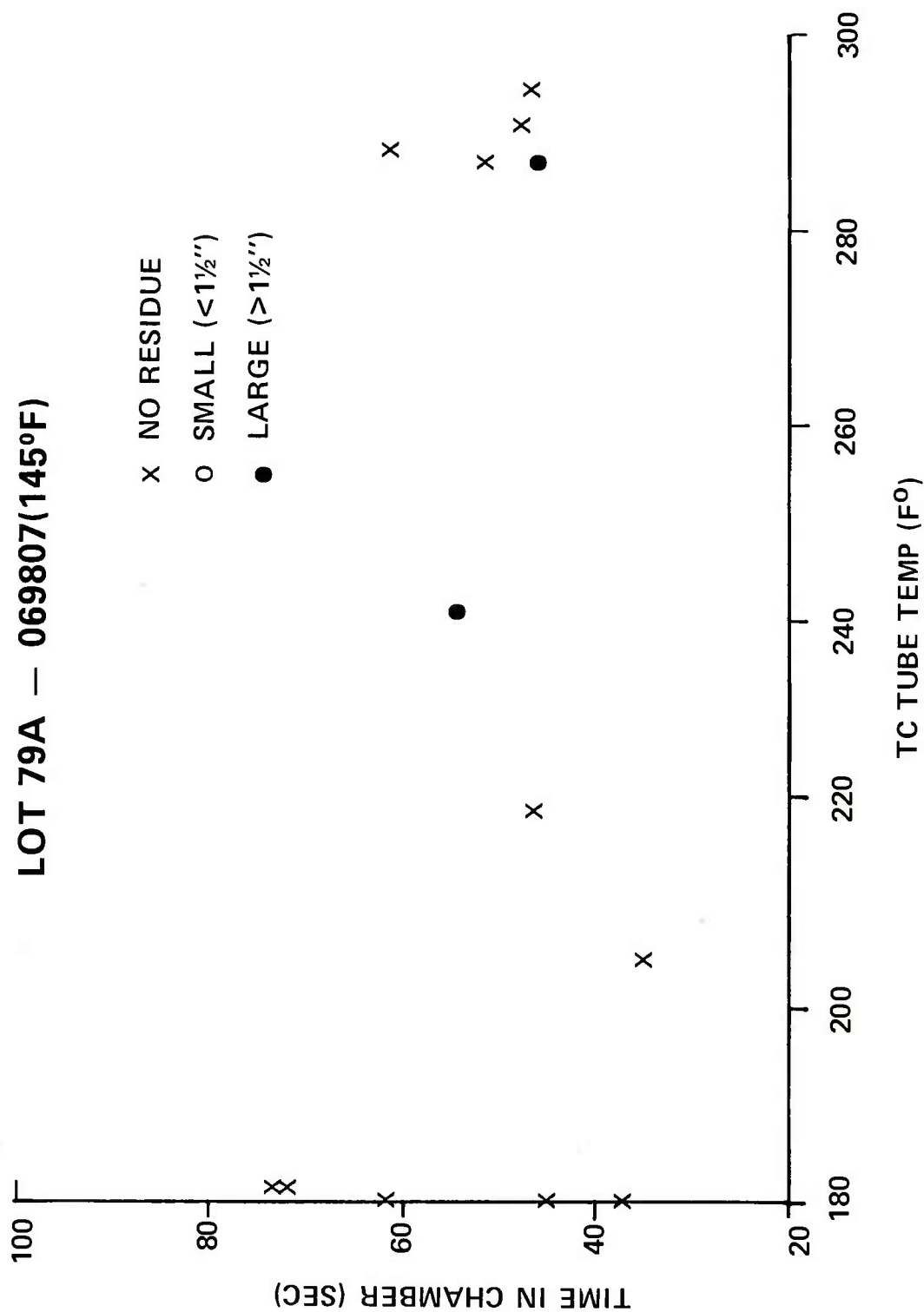


Figure 8. Indramic 170C residue frequency at 63°C (145°F).

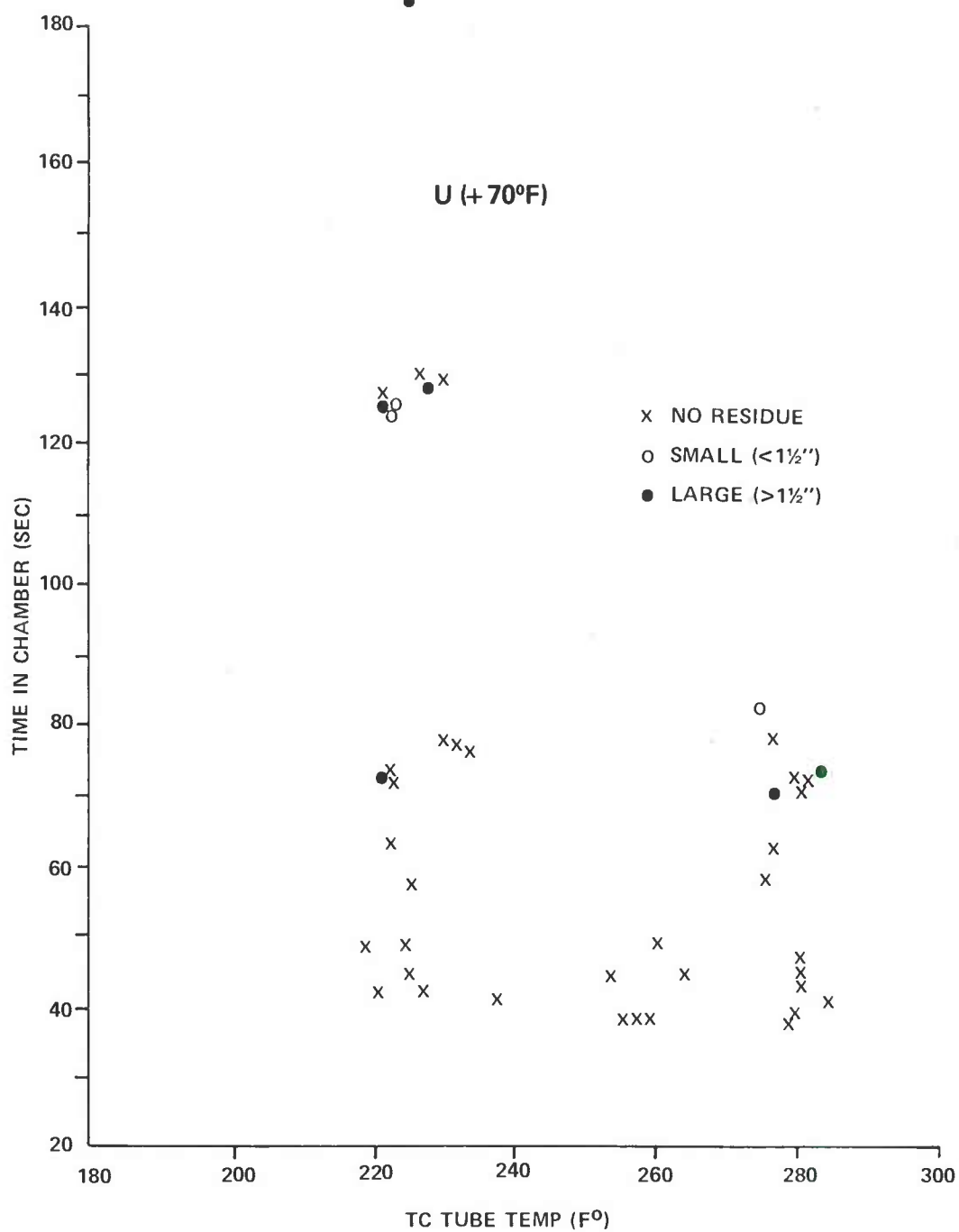


Figure 9. Polywax 655/scrim residue frequency at 21°C (70°F).

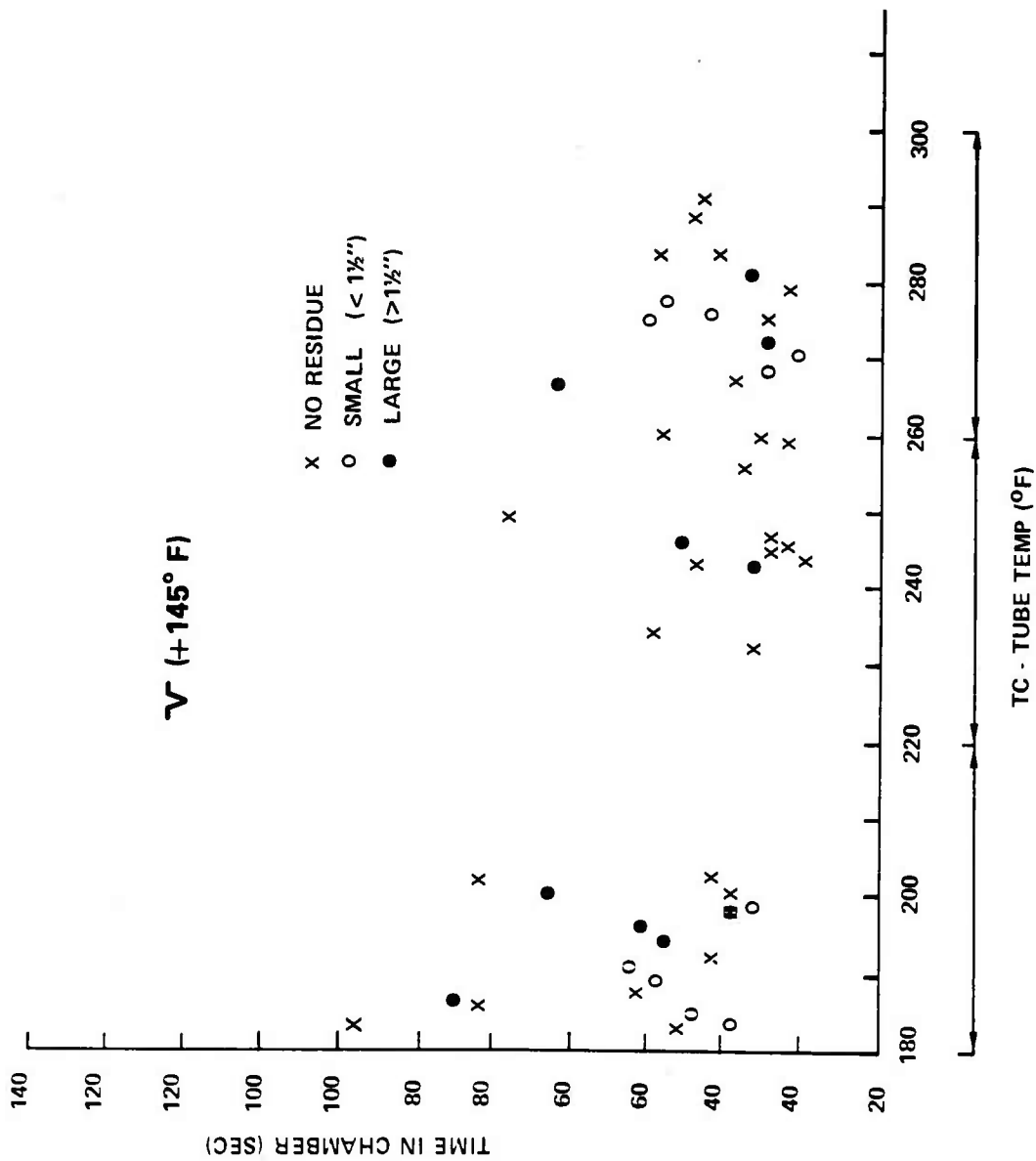


Figure 12. Polywax 655/rayon/lead laminate residue frequency at 63°C (145°F).

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